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Response of the Aerodyne Aerosol Mass Spectrometer to Inorganic Sulfates and Organosulfur Compounds: Applications in Field and Laboratory Measurements

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Abstract

Organosulfur compounds are important components of secondary organic aerosols (SOA). While the Aerodyne high-resolution time-of-flight aerosol mass spectrometer (AMS) has been extensively used in aerosol studies, the response of the AMS to organosulfur compounds is not well-understood. Here, we investigated the fragmentation patterns of organosulfurs and inorganic sulfates in the AMS, developed a method to deconvolve total sulfate into components of inorganic and organic origins, and applied this method in both laboratory and field measurements. Apportionment results from laboratory isoprene photooxidation experiment showed that with inorganic sulfate seed, sulfate functionality of organic origins can contribute ~7% of SOA mass at peak growth. Results from measurements in the Southeastern U.S. showed that 4% of measured sulfate is from organosulfur compounds. Methanesulfonic acid was estimated for measurements in the coastal and remote marine boundary layer. We explored the application of this method to unit mass-resolution data, where it performed less well due to interferences. Our apportionment results demonstrate that organosulfur compounds could be a non-negligible source of sulfate fragments in AMS laboratory and field datasets. A reevaluation of previous AMS

41 measurements over the full range of atmospheric conditions using this method could
42 provide a global estimate/constraint on the contribution of organosulfur compounds.

43

Introduction

Organosulfur compounds have been identified in both laboratory-generated and ambient aerosols.[1-9] It has been suggested that these compounds can comprise a substantial fraction of organic aerosol (OA) mass.[3, 6, 9] Organosulfur compounds are generally of low volatility,[7, 8] and can be an important component of high molecular weight (MW) compounds in ambient aerosols. Due to their surface-active nature and chemical stability,[1, 10, 11] organosulfur compounds can play a potentially important role in altering aerosol physicochemical properties.[5, 12, 13] Organosulfur compounds are also thought to be good tracers for aqueous particle-phase secondary OA (SOA) formation.[14] Given their importance, different methods have been explored to quantify organosulfur compounds in ambient aerosols. Offline methods such as Fourier transform infrared (FTIR) transmission spectroscopy have been used to measure C-O-S functional groups.[15] The difference between total particulate sulfur measured by X-ray emission techniques and water soluble inorganic sulfate measured by ion chromatography (IC) has been used to provide an upper-limit estimation of atmospheric organosulfur compounds.[3, 6, 16, 17] However, this method suffers uncertainties from instrument cross-calibrations.[17] Liquid chromatography-electrospray ionization-tandem mass spectrometry (LC-ESI-MS/MS) is widely used to identify and quantify organosulfur compounds,[5] but the quantification of total organosulfur compounds is limited by the availability of authentic standards.[10, 18] For online methods, Particle Ablation by Laser Mass Spectrometry (PALMS) single particle mass spectrometer has been used to measure certain organosulfur compounds in single particles,[9, 19] but as a single particle mass spectrometer, PALMS suffers from quantification issues.[20]

The high resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS, Aerodyne; henceforth referred to as AMS) has also been used to estimate the lower bound of ambient organosulfur compound concentrations based on the signal intensity of organosulfur ions ($C_xH_yO_zS^+$) and their fractional contributions in pure organosulfur compound standards.[21] However, most sulfate and sulfonate functionalities in organosulfur compounds fragment to $H_xSO_y^+$ ions.[21, 22] Meanwhile, $H_xSO_y^+$ ions in the AMS are often misinterpreted as arising only from inorganic sulfates in subsequent analysis. This potential misattribution can result in an underestimation of organic mass and a corresponding overestimation of inorganic sulfate mass, and it also causes underestimation of S/C. Docherty et al.[23] have shown that when including the S content of organosulfates in elemental analysis calculations, S/C can increase by a factor of 30 for an ambient study. Methanesulfonic acid, which is an important organosulfur compound in marine aerosols,[24, 25] has been quantified with the AMS based on their signature organosulfur fragments (sometimes complemented by PMF analysis),[21, 25-30] which are much more abundant due to the C-S bonding rather than C-O-S bonding, and the smaller size of methanesulfonic acid compared to other organosulfur compounds.[31]

In this study, we developed a method to estimate the concentration of organosulfur compounds based on AMS-measured sulfate mass spectra. 16 standard organosulfur standards (including organosulfates, sulfonates, and sulfonic acids) were tested in the laboratory. Methanesulfonic acid was evaluated and discussed separately from other organosulfur compounds because of its distinctive mass spectrum. We applied this method to both chamber and ambient measurements and discussed their atmospheric implications. Four different AMSs were used in standard calibrations and chamber/ambient

measurements, which will be referred hereafter as GT AMS (Georgia Institute of Technology group), Galway AMS (National University of Ireland Galway group), TROPOS AMS (Leibniz Institute for Tropospheric Research group), and Boulder AMS (University of Colorado-Boulder group) hereafter.

Materials and Methods

Laboratory Characterization of Standard Compounds. The fragmentation patterns of standard compounds were obtained by directly atomizing 10 - 140 μM aqueous solutions of standard compounds into the AMS. The particles were generated by an ultrasonic nebulizer (U-5000AT, Cetac Technologies Inc., Omaha, Nebraska, USA), and passed through a nafion dryer to remove excess water prior to entering the AMS. In this study, 3 inorganic sulfates and 16 organosulfur compounds were tested with the GT AMS (**Table S2**). The 3 inorganic sulfates are ammonium sulfate (AS), acidic AS (1:1 mixture of ammonium sulfate and sulfuric acid), and sodium sulfate (SS). The 16 organosulfur compounds include 4 linear alkyl organosulfate salts (sodium methyl sulfate, sodium ethyl sulfate, sodium n-heptyl sulfate, and sodium n-octyl sulfate), 2 oxygenated organosulfate salts, one containing a carboxylic acid functional group (potassium glycolic acid sulfate) and the other containing a carbonyl functional group (potassium hydroxyacetone sulfate), 6 aromatic organosulfate salts (potassium o-cresol sulfate, potassium p-cresol sulfate, potassium m-cresol sulfate, sodium benzyl sulfate, potassium 4-nitrophenyl sulfate, and potassium 4-hydroxy-3-methoxyphenylglycol sulfate), 2 sulfonate salts (sodium 1-butanesulfonate and sodium benzenesulfonate), and 2 sulfonic acids (methanesulfonic acid and ethanesulfonic acid). Pure sulfuric acid mass spectrum was acquired with the Boulder AMS. Methanesulfonic acid

(MSA) will be discussed separately from other organosulfur compounds due to its unique fragmentation patterns in the AMS. Organosulfate, sulfonate, and sulfonic acid standards tested in this study but excluding MSA will be referred to as OS hereafter.

Structures of standard compounds are shown in **Table S2**. Hydroxyacetone sulfate, glycolic acid sulfate, and benzyl sulfate were synthesized in the laboratory according to the method described in Hettiyadura et al.[18] o-cresol sulfate, p-cresol sulfate, and m-cresol sulfate were synthesized in the laboratory according to the method described in Staudt et al.;[32] the rest of organosulfur standards are commercially available. Among all OS standards evaluated in this work, glycolic acid sulfate (OS-3) is one of the most abundant atmospheric organosulfates quantified so far.[9, 10, 18, 33] Hydroxyacetone sulfate (OS-4), methyl sulfate (OS-1), o-cresol sulfate (OS-7), p-cresol sulfate (OS-8), m-cresol sulfate (OS-9), and benzylsulfate (OS-10) have also been detected in ambient aerosols in prior studies.[18, 32]

Characterization of Chamber-Generated Biogenic SOA and ambient OA. One isoprene photooxidation experiment under low-NO condition and four sets of field measurements conducted by different groups with different AMS were investigated in this study to probe the time variations and abundance of organosulfur compounds in well-controlled single VOC system and in different ambient environments, including biogenic VOC (BVOC) dominated southeastern US measurements (Centreville measurements), MSA abundant coastal and cruise measurements (Mace Head and Polarstern measurements), and high acidity aircraft measurements (WINTER measurements). Details of the experiment and field measurements are presented in the Supporting Information section **S1**.

Four different AMS are included in the discussions, GT AMS (chamber isoprene SOA and Centreville measurements), Galway AMS (Mace Head measurements), TROPOS AMS (Polarstern measurements), and Boulder AMS (WINTER measurements).

Sulfate Apportionment Method

AMS Sulfate Mass Spectra of Standard Compounds. Organosulfates, sulfonates, and sulfonic acids predominantly fragment into separate organic ($C_xH_yO_z$) and sulfate fragments (SO_x) rather than organosulfur fragments ($C_xH_yO_zS$) in the AMS (**Figure S1**), suggesting that most C-O-S (corresponding to organosulfates) and C-S (corresponding to sulfonates and sulfonic acids) bonds are not retained after vaporization and ionization. Sulfonate and sulfonic acid molecules do not contain a sulfate functional group, but the $H_xSO_y^+$ fragments they produce in the AMS would be counted as sulfate concentrations in standard data processing. Therefore, these $H_xSO_y^+$ fragments produced by sulfonates and sulfonic acids will still be referred to as "sulfate" fragments hereafter. For all OS tested in this study, organosulfur fragments only contribute 0.02 - 4% to the total signal, depending on the MW, structure, and bonding types (**Figure S1**). Generally, OS with smaller MW of carbon backbones tend to produce a larger fraction of organosulfur fragments, but the structure of the carbon backbones and bonding types may also play a role. For instance, methyl sulfate (OS-1, $H_3C\text{-}O\text{-}SO_3^-$) and MSA ($H_3C\text{-}SO_3^-$) have the same carbon backbone, but MSA retains a much higher portion of organosulfur fragments (16%) because of the different bond types between sulfate/sulfonate groups and the carbon backbones. This difference becomes negligible when one more methyl group is added to the carbon backbone (**Figure S1,** ethyl sulfate (OS-2) and ethanesulfonic acid (OS-15)). Phenyl sulfonates produce a higher fraction

of organosulfur fragments compared to other OS with similar MW of carbon backbones (**Figure S1,** benzenesulfonate (OS-14)), possibly due to the stabilization by resonance between benzene ring and sulfonate group.[31] Due to their small signals, the organosulfur fragments are subject to interference by stronger neighboring signals in the most common V-mode resolution (m/dm~2500) for the AMS when sampling complex matrices such as ambient aerosols, posing a barrier to estimating OS mass only by organosulfur fragments. In contrast, the major sulfate fragments have strong signals and can be well fitted (**Figure S2-S4**). Consequently, we focused on using the sulfate fragments to understand the fragmentation patterns of different inorganic sulfates and organosulfur compounds in the AMS.

The typical V-mode AMS high-resolution sulfate mass spectra of AS, MSA, SS, and an OS standard (sodium benzyl sulfate, OS-10) are shown in **Figure 1(a)**. The spectra obtained in this study show a very similar pattern to those reported elsewhere.[21, 27, 28, 34] Among all the fragments produced by the fragmentation of these different sulfate/sulfonate-containing compounds, the main ions are SO^+, SO_2^+, SO_3^+, HSO_3^+, and $H_2SO_4^+$.[35] Here, we referred to the sum of these five ions as ΣHSO and normalized each of the five ions to ΣHSO. The normalization can be expressed by equations (1) - (6):

$$\Sigma HSO = SO^+ + SO_2^+ + SO_3^+ + HSO_3^+ + H_2SO_4^+ \quad (1)$$

$$f_{SO} = \frac{SO^+}{\Sigma HSO} \quad (2)$$

$$f_{SO_2} = \frac{SO_2^+}{\Sigma HSO} \quad (3)$$

$$f_{SO_3} = \frac{SO_3^+}{\Sigma HSO} \quad (4)$$

$$f_{HSO_3} = \frac{HSO_3^+}{\Sigma HSO} \quad (5)$$

$$f_{H_2SO_4} = \frac{H_2SO_4^+}{\Sigma HSO} \quad (6)$$

The normalized SO^+, SO_2^+, SO_3^+, HSO_3^+, and $H_2SO_4^+$ abundance is shown in **Figure 1(b)**. For all standards, smaller ions like SO^+, SO_2^+ and SO_3^+, account for most of the ΣHSO signals, which can be explained by the extensive thermal decomposition during vaporization and fragmentation after electron impact (EI) ionization. Meanwhile, the HSO_3^+ fragment is only produced by MSA and AS (at different relative abundances), and $H_2SO_4^+$ fragment is exclusively produced by AS. These observations can be explained by their different chemical structures. For organosulfates, it takes less energy to break the O-S bond than the C-O bond,[36] so it is more likely for the organic part to retain the oxygen during fragmentation and result in small sulfate fragments with at most three oxygens. For MSA, the sulfur molecule is bonded to three oxygens so that the $H_2SO_4^+$ ion cannot be produced, while the HSO_3^+ ion can be produced by breaking the C-S bond. For ammonium sulfate, sulfate decomposes to either dehydrated SO_3 ($+H_2O$) or intact H_2SO_4,[37] and the water signal produced due to the dehydration process is calculated based on an empirical sulfate fragmentation table (**Table S4**).[37] For the other sulfate/sulfonate-containing species discussed in this study (MSA, OS, and SS), there is no pathway to produce water fragments, therefore a sulfate fragmentation table without water fragments was used for these species (**Table S4**).

The distinctive HSO_3^+ and $H_2SO_4^+$ ion fractions in different standard compounds provide the basis for our method of distinguishing different types of sulfate/sulfonate-containing compounds. **Figure 1(c)** shows the $f_{H_2SO_4}$ vs. f_{HSO_3} for all standard compounds.

The four types of standards (AS, OS, SS, and MSA) together defined a triangle-shaped space, with OS and SS occupying indistinguishable regions in this space. There are some variations in f_{HSO_3} and $f_{H_2SO_4}$ among all OS (**Table S3**), but the variations are small, thus the average value for all OS was used hereafter. Different types of inorganic sulfates and organosulfur compounds fall into different regions in this space and thus can be distinguished. The relative contribution from each type of sulfate/sulfonate-containing compounds can be estimated for any point in this space. The mass spectra of AS and MSA obtained by the Galway AMS, TROPOS AMS, and Boulder AMS are also shown in **Figure 1(c)**. The differences in the same type of compounds among different AMS likely arise from instrument-to-instrument and time-to-time variability. Therefore, when applying the apportionment method, calibrations with SS/OS, AS, and MSA standards to define the triangle region are required for the particular instrument and time period. In addition, calibrations of RIE for the standard species are required for accurate quantification.

Development of Sulfate Apportionment Method. Based on the different f_{HSO_3} and $f_{H_2SO_4}$ for different types of sulfate/sulfonate-containing compounds, we developed an approach to deconvolve total sulfate signals into components of inorganic and organic origins. Based on the f_{HSO_3} and $f_{H_2SO_4}$ values determined for pure standard compounds in the laboratory, the measured HSO_3^+, $H_2SO_4^+$, and ΣHSO can be expressed as:

$$\mathrm{HSO_{3,meas}} = f_{HSO_3,AS,standard} \times \Sigma\mathrm{HSO_{AS}} + f_{HSO_3,OS/SS,standard} \times \Sigma\mathrm{HSO_{OS/SS}} + f_{HSO_3,MSA,standard} \times \Sigma\mathrm{HSO_{MSA}} \quad (7)$$

$$\mathrm{H_2SO_{4,meas}} = f_{H_2SO_4,AS,standard} \times \Sigma\mathrm{HSO_{AS}} + f_{H_2SO_4,OS/SS,standard} \times \Sigma\mathrm{HSO_{OS/SS}} + f_{H_2SO_4,MSA,standard} \times \Sigma\mathrm{HSO_{MSA}} \quad (8)$$

$$\Sigma\mathrm{HSO_{meas}} = \Sigma\mathrm{HSO_{AS}} + \Sigma\mathrm{HSO_{OS/SS}} + \Sigma\mathrm{HSO_{MSA}} \quad (9)$$

The subscript "$_{meas}$" denotes the measured mass concentration of sulfate fragments, and the subscript "$_{standard}$" denotes measured fractions of standard compounds. ΣHSO_{AS}, $\Sigma HSO_{OS/SS}$, and ΣHSO_{MSA} are ΣHSO for AS, OS or SS, and MSA, respectively, which can be solved by:

$$\begin{bmatrix} \Sigma HSO_{AS} \\ \Sigma HSO_{OS/SS} \\ \Sigma HSO_{MSA} \end{bmatrix} = \begin{bmatrix} f_{HSO_3,AS,standard} & f_{HSO_3,OS/SS,standard} & f_{HSO_3,MSA,standard} \\ f_{H_2SO_4,AS,standard} & f_{H_2SO_4,OS/SS,standard} & f_{H_2SO_4,MSA,standard} \\ 1 & 1 & 1 \end{bmatrix}^{-1} \begin{bmatrix} HSO_{3,meas} \\ H_2SO_{4,meas} \\ \Sigma HSO_{meas} \end{bmatrix} \quad (10)$$

Afterwards, the fractions of ΣHSO in AMS total sulfate signals (i.e., $\left(\frac{\Sigma HSO}{\text{total sulfate}}\right)_{standard}$) acquired for each type of species during the calibrations will be used to convert ΣHSO signals from above calculations to total sulfate signals.

For OS and SS, they are indistinguishable in the f_{HSO_3} vs. $f_{H_2SO_4}$ space, but their relative contributions to total sulfate in ambient data can be highly dependent on the measurement locations. SS is considered as a refractory species and cannot be completely vaporized at 600 ^oC (default AMS vaporizer temperature).[38] As a result, for typical continental sites, SS signals may be a minor component compared to OS. For coastal and cruise measurements, SS cannot be neglected due to its abundance. In the following discussion, we will treat $\Sigma HSO_{OS/SS}$ resolved for a continental site (Centreville) as dominantly from OS (except for a short period of crustal events), and for coastal or marine measurements (Mace Head and Polarstern), we will treat OS and SS as one component, i.e., the summation of OS and SS.

Laboratory Calibration of Sulfate RIE. The sulfate RIE (relative ionization efficiency of the species of interest relative to nitrate)[35] in the AMS (RIE_{SO4}) can be calibrated with pure ammonium sulfate.[39] The default RIE_{SO4} of 1.2 was used for ammonium sulfate in this study because this calibration was not performed for the majority of the field studies discussed here. Our two-year records (2017 - 2018) of RIE_{SO4} on the GT AMS is 1.20 ± 0.15, validating that 1.2 is a good estimation. The RIE_{SO4} of organosulfate compounds can be lower than that of ammonium sulfate, since during the fragmentation and ionization processes, the electronegative sulfate/sulfonate groups have a reduced tendency to retain the charge.[23, 40, 41] The RIE_{SO4} was determined for two commercially available organosulfur compounds (MSA and ethyl sodium sulfate (OS-2)) with the GT AMS. Size-selected (300 nm) pure MSA (or OS-2) was atomized to the AMS and a condensation particle counter (CPC; TSI 3775) simultaneously. Sulfate concentration based on particle number was calculated by:

$$[\mathrm{SO_4}]_{\mathrm{CPC}} = \frac{n_{CPC}\pi\rho D_p^3}{6} f_{SO_4,formula} \qquad (11)$$

where n_{CPC} is the particle number concentration measured by CPC, ρ is the density of organosulfur compounds, D_p is the selected particle diameter, and $f_{SO_4,formula}$ is the sulfate functionality mass fraction according to the compound formula (e.g., 81/96 for MSA). The collection efficiency (CE) of 1 was applied to AMS data. Viscosity measurements of organosulfur compounds are lacking in literature. Here we assumed that MSA and OS-2 particles are of low viscosity given their low MW,[42, 43] while uncertainty regarding this assumption exits. A RIE_{SO4} of 0.77 was calculated for MSA and a RIE_{SO4} of 0.82 is calculated for OS-2. The reason for the lower RIE_{SO4} for MSA is because a higher fraction of organosulfur

256 fragments was produced in the fragmentation process of MSA compared to OS-2 (**Figure S1**),
257 and these fragments were not accounted in the sulfate concentration in equation (11). For
258 the subsequent analysis, we tentatively applied an RIE of 0.8 to sulfate produced by
259 organosulfur compounds. A default RIE of 1.2 was applied to "AS sulfate".

260 Results and Discussion

261 **Sulfate Apportionment for Laboratory-Generated Binary Mixtures.** The sulfate
262 apportionment method was first validated with laboratory-generated aerosols of known
263 compositions. Two different types of standard compound solutions were pre-mixed and
264 nebulized into an AMS (GT AMS). Particles with a mobility diameter of 300 nm were selected.

265 We first tested the mixture of AS with MSA. MSA and AS were dissolved in DI water
266 in different molar ratios (3:1, 2:1, 1:1, 1:2, 1:3). The mixture solution was immediately
267 nebulized into the AMS. After obtaining ΣHSO_{MSA} and ΣHSO_{AS} by equation (10), total sulfate
268 signals by MSA ("MSA sulfate") and AS ("AS sulfate") were calculated by:

269 $$SO_{4,MSA} = \frac{\Sigma HSO_{MSA}}{RIE_{SO4,MSA}} \left(\frac{\Sigma HSO}{SO_4} \right)_{MSA,standard} \quad (12)$$

270 $$SO_{4,AS} = \frac{\Sigma HSO_{AS}}{RIE_{SO4,AS}} \left(\frac{\Sigma HSO}{SO_4} \right)_{AS,standard} \quad (13)$$

271 **Figure S6(a)** shows "MSA sulfate" to "AS sulfate" molar ratio calculated by
272 apportionment method as a function of MSA to AS molar ratio in the particles. The MSA to
273 AS ratio in the particles was assumed to be the same as that in the solution.[44-46] MW of 98
274 g/mol and 81 g/mol are used for "AS sulfate" and "MSA sulfate", respectively, to calculate

their molar ratios. The calculated "MSA sulfate" to "AS sulfate" ratio agreed well with particle compositions (slope $= 0.97 \pm 0.02$).

A similar binary mixture apportionment analysis was carried out for mixtures of AS and OS standards. The results of AS and ethanesulfonic acid (OS-15) mixtures are shown in **Figure S6(b)**. Similarly, the calculated sulfate produced by OS ("OS sulfate") to "AS sulfate" ratio is highly correlated with particle composition. The slope is lower than 1 (0.88 ± 0.04) but still within the uncertainty of AMS measurements.

Effect of Particle Acidity on AS Fragmentation Pattern. Considering marine and stratospheric aerosols are rich in sulfuric acid,[25, 47] and the particle pH is low in the southeastern U.S.,[48] we investigated the fragmentation pattern of acidic AS. Acidic sulfate (1:1 mixture of ammonium sulfate and sulfuric acid) was tested with the GT AMS, and pure sulfuric acid was tested with the Boulder AMS. The results are shown in **Figure 2(a)**. All f_{HSO_3} and $f_{H_2SO_4}$ are normalized to those of AS from the specific AMS to minimize the influence from instrument-to-instrument variability, so that AS would always be at point (1,1) in the $f_{H_2SO_4}$ vs. f_{HSO_3} space. Acidic AS shows a similar fragmentation pattern to AS, with a slightly higher production of HSO_3^+ and $H_2SO_4^+$ fragments (**Table S3** and **Figure 2(a)**). However, pure sulfuric acid shows almost twice higher fractions of HSO_3^+ and $H_2SO_4^+$ fragments (**Figure 2 (a)**) compared to AS. We speculate that the reason is that a much larger fraction evaporates intact for pure sulfuric acid, compared to the fraction of the sulfate that evaporates as sulfuric acid for AS and acidic AS, and dehydration is more likely to happen for sulfate salts than sulfuric acid.[37, 49] Since vaporization equilibrium between H_2SO_4 and SO_3 +

296 H_2O can shift with changing temperature, a precise temperature control of the AMS vaporizer
297 and a MS tuning that favors a non-mass dependent response are necessary.[39]

298 The Boulder AMS was also deployed in the WINTER aircraft campaign,[50] where it
299 intercepted a strong coal-fired power plant plume (~ 50 ppb SO_2). As shown in **Figure 2(b)**,
300 the estimated particle pH (calculated with the E-AIM model[51-53]) decreased rapidly to -1 in
301 the core of the plume. The highest f_{HSO_3} and $f_{H_2SO_4}$ values in the plume are 72% and 21%
302 higher, respectively, compared to pure AS from the same AMS. In this strong plume, the
303 sulfate concentration is an order of magnitude higher than ammonium, nitrate, and organics
304 concentrations, thus the change in f_{HSO_3} and $f_{H_2SO_4}$ is attributed to the near sulfuric acid
305 conditions and very high acidity. The shifts in f_{HSO_3} and $f_{H_2SO_4}$ to values outside the region
306 defined by the OS/SS-AS-MSA triangle suggest that caution is needed when applying the
307 apportionment method to data obtained under high acidity (near pure H_2SO_4, molar ratio of
308 NH_4:$SO_4 < 0.8$) conditions. Nevertheless, for ground studies the ambient particles are less
309 acidic than pure sulfuric acid particles in most cases.[54-58]

310 **Sulfate Apportionment for Chamber-Generated Isoprene SOA.** Organosulfates can be
311 formed in isoprene photooxidation reactions.[2, 59] Here, we applied the sulfate apportionment
312 method to quantify OS formation in an isoprene photooxidation experiment. [60] The reaction
313 profile is shown in **Figure 3**. The increase in total sulfate concentration as SOA started to
314 form is likely due to increase in collection efficiency (CE) with the condensation of
315 organics.[61, 62] We assumed all O-S bonds in C-O-S structures (corresponding to
316 organosulfates) are broken. Thus no organosulfur fragments are produced, and
317 sulfate/sulfonate functionality MW is 80 g/mol (corresponding to SO_3) for all OS. With these,

318 we estimated that 7% of AS seed has become organosulfate as SOA reaches peak growth, and
319 the "OS sulfate" could contribute to 7% of total SOA. $C_xH_yO_zS^+$ ions only account for 0.07% of
320 total SOA, consolidating our assumption that almost all O-S bonds in C-O-S structures are
321 broken to form "OS sulfate". Prior studies have shown that the formation of isoprene-epoxydiol
322 (IEPOX) organosulfate (one of the abundant isoprene-derived organonsulfates) is strongly
323 enhanced in the presence of acidic sulfate seed.[2, 59, 63-66] As our chamber experiment was conducted
324 under dry conditions with ammonium sulfate seed, the contribution of organosulfates to total
325 organic aerosols is expected to be lower than those under humid acidic conditions.[2, 59]

326 **Application to Field Measurements for OS Estimation.** We applied the sulfate
327 apportionment method to the SOAS data from Centreville to deconvolve sulfate from AS, OS,
328 and MSA, respectively. The average "OS sulfate" mass is 0.12 μg/m^3 for the whole campaign,
329 which means that 4% of measured sulfate is from OS. We note that there are some negative
330 values (6% of all the data) in the calculated "OS sulfate" concentration, which is due to data
331 points falling outside the AS-MSA line in the triangle (**Figure S7(a)**), as expected due to
332 measurement noise. Our apportionment result is consistent with recent airborne and ground
333 measurements in the same region. Liao et al. quantified IEPOX-sulfate using PALMS during
334 flight measurements and determined that it accounted for ~5% of the total sulfate mass
335 measured by AMS.[9] Hu et al. also indicated that IEPOX-sulfate accounted for ~5% of total
336 sulfate mass for SOAS measurements.[67] Previous study by Guo et al.[48] showed that AMS total
337 sulfate is 20% higher than inorganic sulfate measured by particle-into-liquid-sampler
338 coupled to an ion chromatograph (PILS-IC) during SOAS. After excluding the OS sulfate
339 calculated from our apportionment method, the resulting AMS "AS sulfate" shows a better
340 agreement (slope = 0.97) with PM_1 inorganic sulfate measured by PILS-IC (**Figure 4(a)**).

We also compare our OS with speciated organosulfur compounds quantified in $PM_{2.5}$ filter samples collected at Centreville during SOAS, using offline hydrophilic interaction liquid chromatography (HILIC) and a triple quadrupole mass spectrometer (TQD MS) against authentic standards.[68] We focus on OS compounds that are both used in the apportionment method development in this study and quantified in the filter analysis. The "OS sulfate" time series calculated by sulfate apportionment method is shown in **Figure 4(b)**, together with total sulfate measured by the AMS,[69, 70] methyl sulfate, glycolic acid sulfate and hydroxyacetone sulfate quantitatively measured by offline HILIC-TQD,[68] and isoprene-OA resolved by PMF.[69, 70] The AMS "OS sulfate" shows a moderate correlation ($R = 0.52$) with speciated organosulfur compounds measured by offline HILIC-TQD. Two periods 6/17/2013 - 6/18/2013 and 6/24/2013 - 6/28/2013 are excluded when calculating the R value, because these two periods overlap with the crustal events when mineral cations are abundant and the contribution of SS is not negligible.[71] For the "OS sulfate" spike on 6/26/2013, we speculated that it is due to the overlap of crustal event with strong isoprene-related OS formation. Further, we compared "OS sulfate" with AMS isoprene-OA factor under different isoprene-OA abundances to study the role of isoprene-derived OS at Centreville. As shown in **Figure 4(c)**, the correlation between "OS sulfate" and isoprene-OA is enhanced as the fraction of isoprene-OA in total OA increases. The improved correlation between "OS sulfate" and isoprene-OA as isoprene-OA fraction increases is consistent with isoprene-derived OS being an important source of OS at Centreville in summer when isoprene is abundant.[68] Such enhancement in correlation is not observed for other OA factors (**Figure S8**), suggesting that even if other factors may contribute to OS, they are not the major sources.

A recent new study characterized 12 types of organosulfur compounds in filter samples of $PM_{2.5}$ collected from SOAS.[72] The sulfate mass associated with these 12 organosulfates over the studied period averaged 0.37 μg/m^3, with 2-methyltetrol sulfate accounting for 80% of the "OS sulfate" mass. These filter results imply that total "OS sulfate" could account for 16% of the total sulfate mass, which is higher than our estimation and prior studies by Liao et al.[9] and Hu et al..[67] Two instruments measuring particles of different sizes (PM_1 by the AMS and $PM_{2.5}$ by filter) and uncertainties in different instrument/measurement techniques likely contribute to the different observations. In this study, we cannot exclude the possibility that the fragmentation pattern of 2-methyltetrol sulfate in the AMS is different from other OS standards. Future work is warranted to expand the analysis to encompass an even wider suite of OS standards as they become available and characterize OS sulfate measured by different techniques.

Application to Field Measurements for MSA Estimation. For measurements at coastal sites and from cruises, we focused on resolving MSA time variation for Mace Head and Polarstern measurements, in a similar manner to OS estimation, using 96 g/mol as MSA MW and 81 g/mol as sulfonic acid functionality MW.

Previous studies have reported the quantification of MSA with the AMS by a well-developed signature fragments method[21, 25-2921, 25-2921, 25-2921, 25-2921, 25-2921, 25-29] based on ions such as $CH_3SO_2^+$, $CH_4SO_3^+$, etc.,[21, 25-29] which are almost solely produced by MSA. Based on the fragmentation pattern of the pure MSA standard, ambient MSA concentration can be calculated using the intensity of signature fragments and their relative contributions in pure MSA. Here, we compared MSA concentration calculated by the signature fragments method

and sulfate apportionment method presented in this study. The results for Mace Head and the RV Polarstern measurements are shown in **Figure 5**. For both datasets, the MSA concentration estimated by the two methods shows good correlation ($R^2 = 0.675$ for Mace Head data, and $R^2 = 0.710$ for Polarstern data). Compared to the signature fragments method, the average concentration estimated by sulfate apportionment method is higher by 30% for Mace Head measurements and 150% for Polarstern measurements. The reason is currently unknown, but a possible cause could be that the high acidity of submicron marine aerosols[73, 74] affects sulfate fragmentation pattern as discussed above. For instance, for the Polarstern measurements, even accounting for the presence of large amount of sea salt sulfate, most data points have higher fractions of HSO_3^+ and $H_2SO_4^+$ fragments than the AS standard (**Figure S7(c)**). Meanwhile, some data points fall outside the OS/SS-AS line in the triangle (**Figure S7(b), (c)**), resulting in negative concentrations in MSA estimation (**Figure 5**), which requires further investigation. Nevertheless, this shows that the sulfate apportionment method is capable of determining the presence of MSA and its approximate concentration, and of approximately separating the MSA contribution from that of AS and OS species.

Implications. In this study, a novel sulfate apportionment method was developed for AMS analysis. We showed that sulfate fragments originated from organosulfur compounds can be resolved from those of inorganic sulfate based on their different sulfate fragmentation patterns, providing insights into the quantity and time variations of organosulfur compounds in the atmosphere. The advantage of this method is that the contribution of "AS sulfate", "OS/SS sulfate", and "MSA sulfate" can be directly estimated using AMS measurements with high time resolution. One thing to note is that the sulfate apportionment

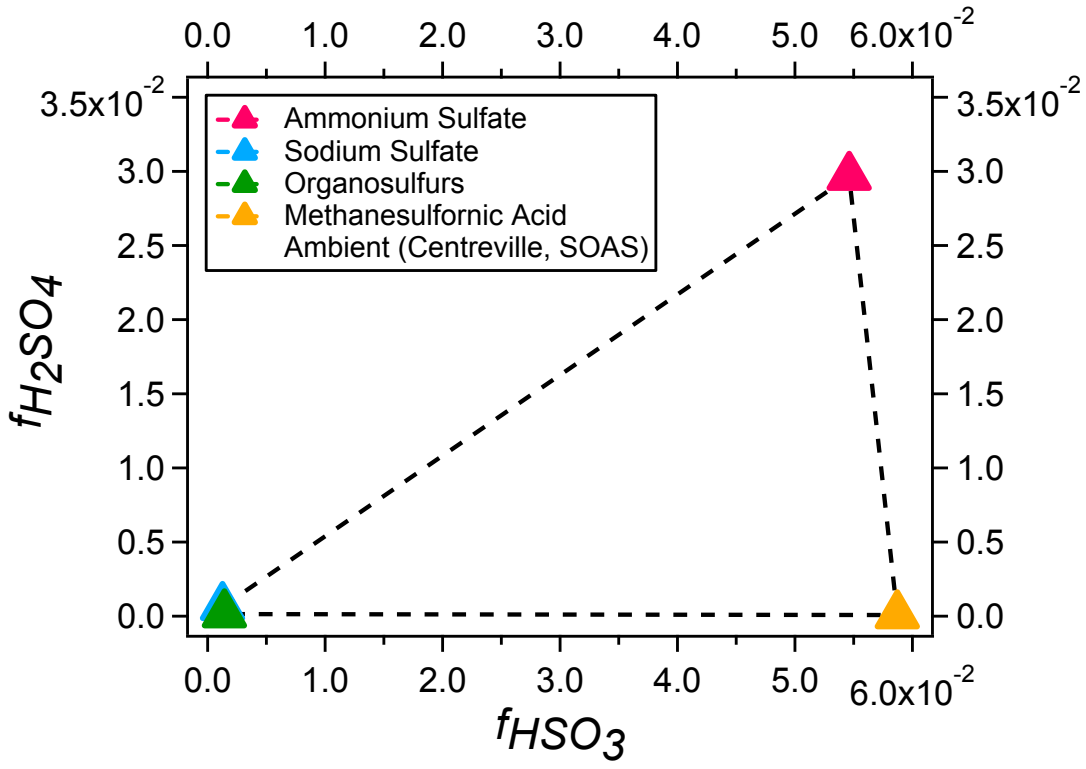
409 method only estimates the mass concentration of sulfate/sulfonate functionalities in
410 organosulfur molecules. The estimation of total OS contribution can be dependent on a good
411 estimation of OS MW.

412 We note that there are several limitations of this study. First, while we have
413 considered an extensive set of atmospherically relevant OS standards, given the variety and
414 complexity of atmospherically relevant organosulfur compounds, additional standards
415 should be evaluated to explore the robustness of the fragmentation patterns of organosulfur
416 compounds presented here. Second, we found that the sulfate fragmentation pattern can be
417 very different under high acidity, making this method not directly applicable under near
418 sulfuric acid conditions, though such extreme particle acidity is not common in typical
419 continental surface measurements. Third, when data points fall outside the triangular region
420 defined by OS/SS-AS-MSA, the estimated concentrations (either OS/SS, AS, or MSA,
421 depending on where the data point falls) could be negative. As this will always occur to some
422 degree due to the impact of random noise, averaging of longer data periods may be more
423 meaningful under low concentration conditions.

424 Currently, the AMS sulfate is often misinterpreted as being entirely inorganic sulfate.
425 Here, we applied the sulfate apportionment method to both chamber and ambient
426 measurements. Our apportionment results clearly demonstrate that organosulfur
427 compounds could be a non-negligible source of sulfate fragments in the AMS. Future studies
428 need to take this into account when reporting organic and inorganic mass concentrations
429 from AMS measurements. In addition to high-resolution (HR) analysis, we also explored the
430 plausibility of deconvolving AMS sulfate for unit mass resolution (UMR) measurements in

431 the Supporting Information section **S3**. Overall, quantitative measurements of organosulfur
432 compounds with high-time resolution will allow for improved constraints of their abundance
433 in different environments and help advance the understanding of organosulfur compounds
434 formation and related chemical processes in the atmosphere.

435



Abstract Graphic

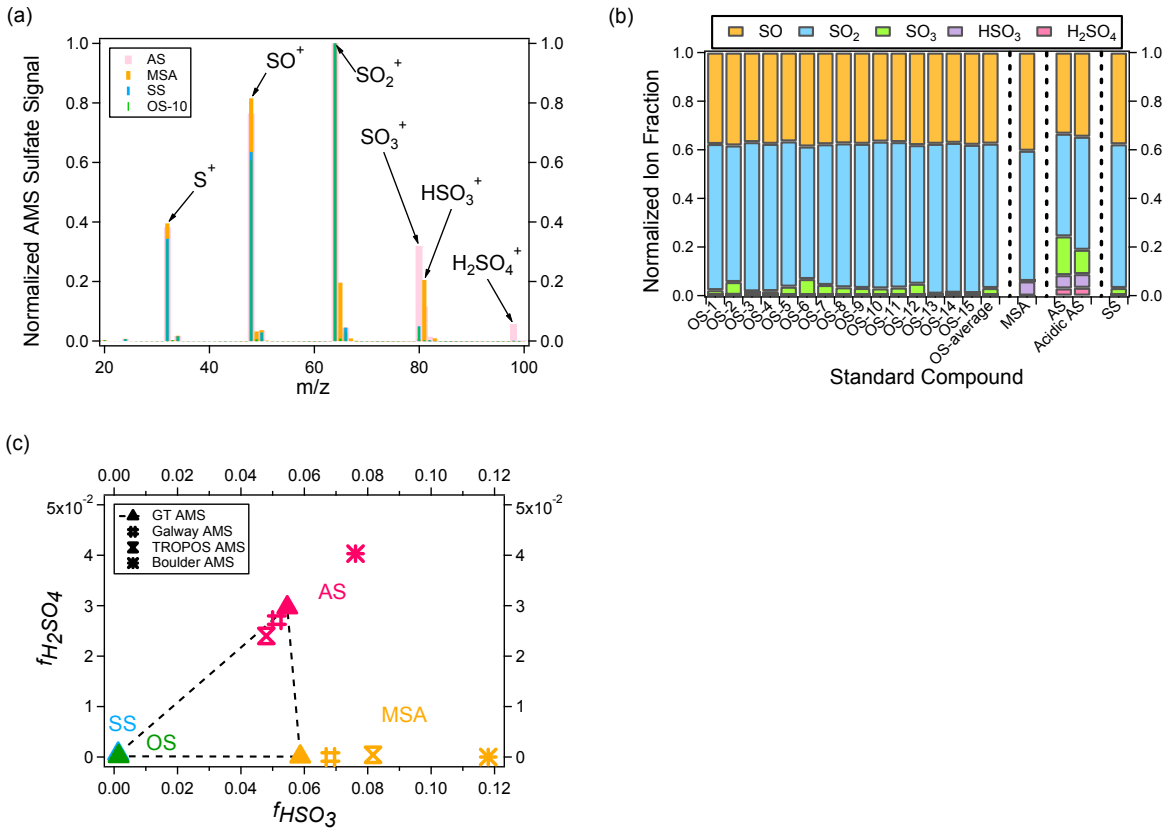


Figure 1 (a) Typical normalized sulfate mass spectra of organosulfur compounds (OS; OS-10 refers to sodium benzyl sulfate in **Table S2**), ammonium sulfate (AS), methanesulfonic acid (MSA), and sodium sulfate (SS), not including water fragments. (b) Mass fraction of main familyHSO ions. (c) $f_{H_2SO_4}$ vs. f_{HSO_3} for standard compounds. For OS, the shown f_{HSO_3} and $f_{H_2SO_4}$ are averages for all 15 OS. OS and SS standard calibrations were only performed with the GT AMS, while MSA and AS standard calibrations were performed with multiple AMS.

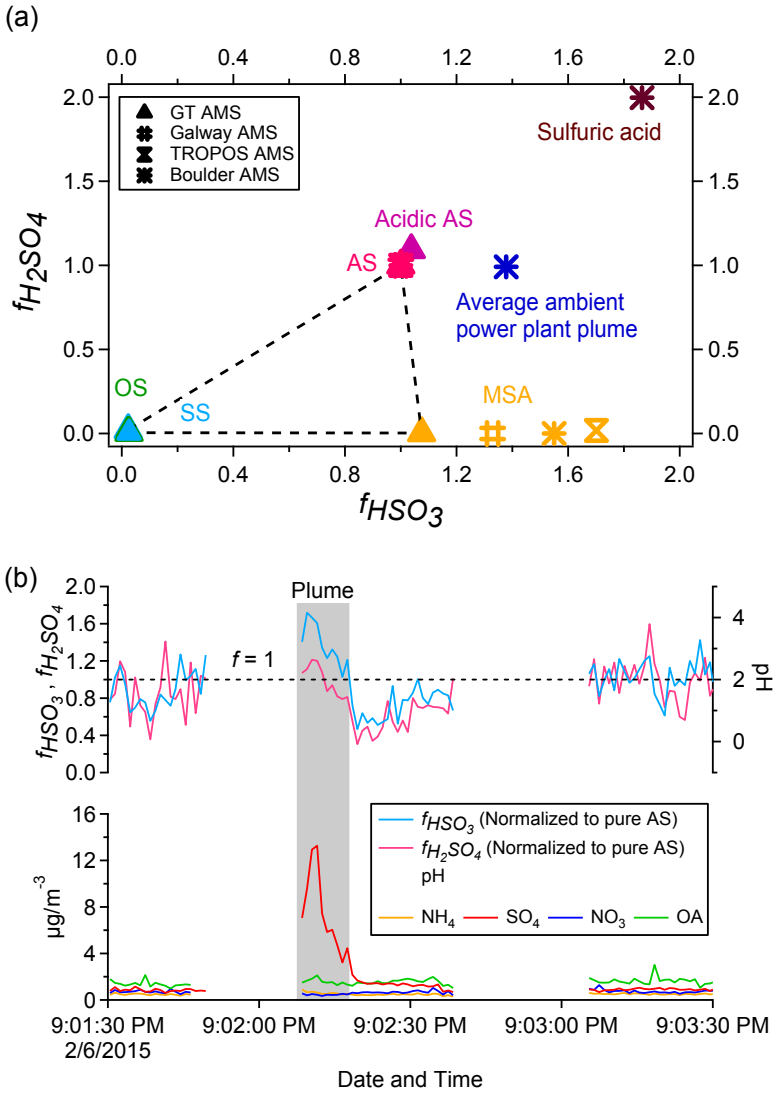


Figure 2 (a) $f_{H_2SO_4}$ vs. f_{HSO_3} for standard compounds and the strong SO_2 plume (average data) during the WINTER aircraft campaign. Both f_{HSO_3} and $f_{H_2SO_4}$ are normalized to those of AS from the specific AMS, so that AS would always be at (1,1) (b) Evolution of f_{HSO_3} and $f_{H_2SO_4}$ (normalized to pure AS), pH, and AMS species in a power plant plume in WINTER aircraft campaign. Acidic AS is 1:1 mixture of ammonium sulfate and sulfuric acid.

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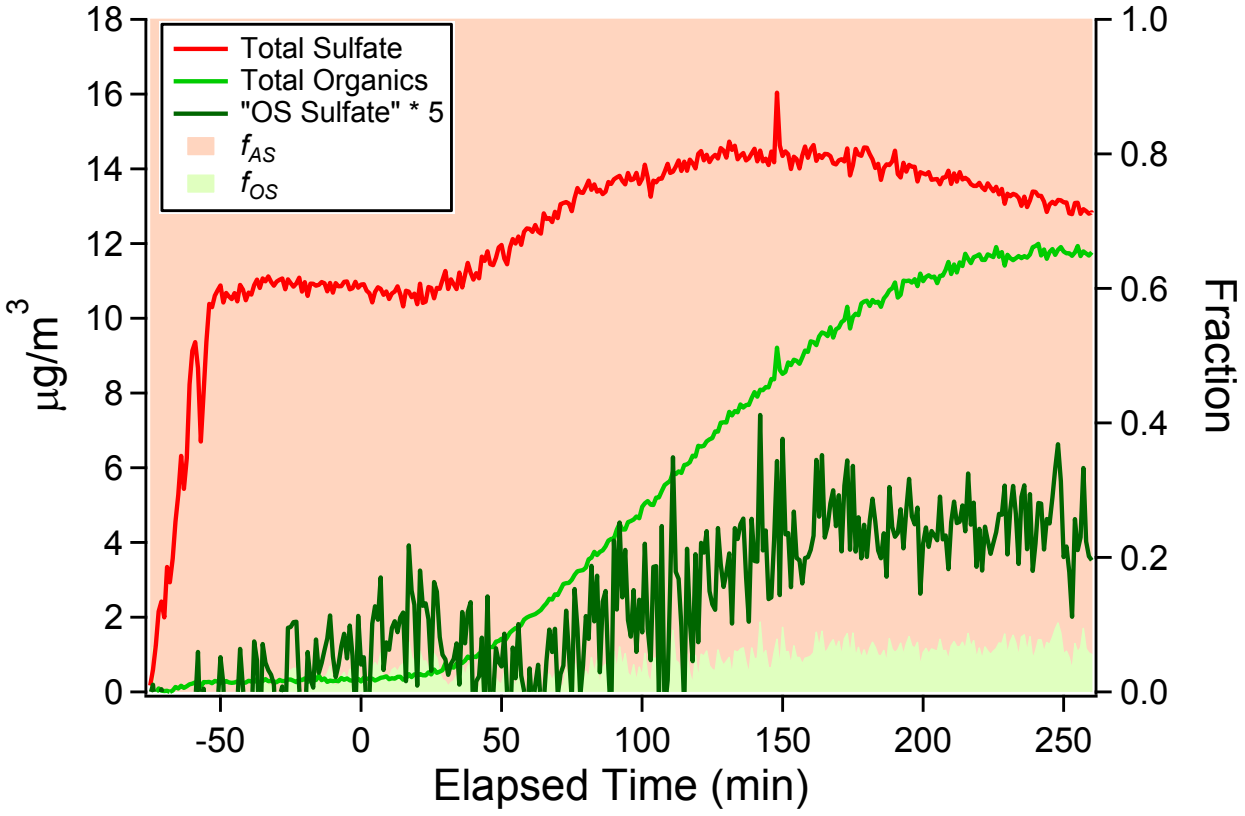


463

464 **Figure 3** Reaction profile of the chamber isoprene photooxidation experiment. The f_{AS} and

465 f_{OS} refer to fraction of "AS sulfate" and "OS sulfate", respectively, in total sulfate.

466

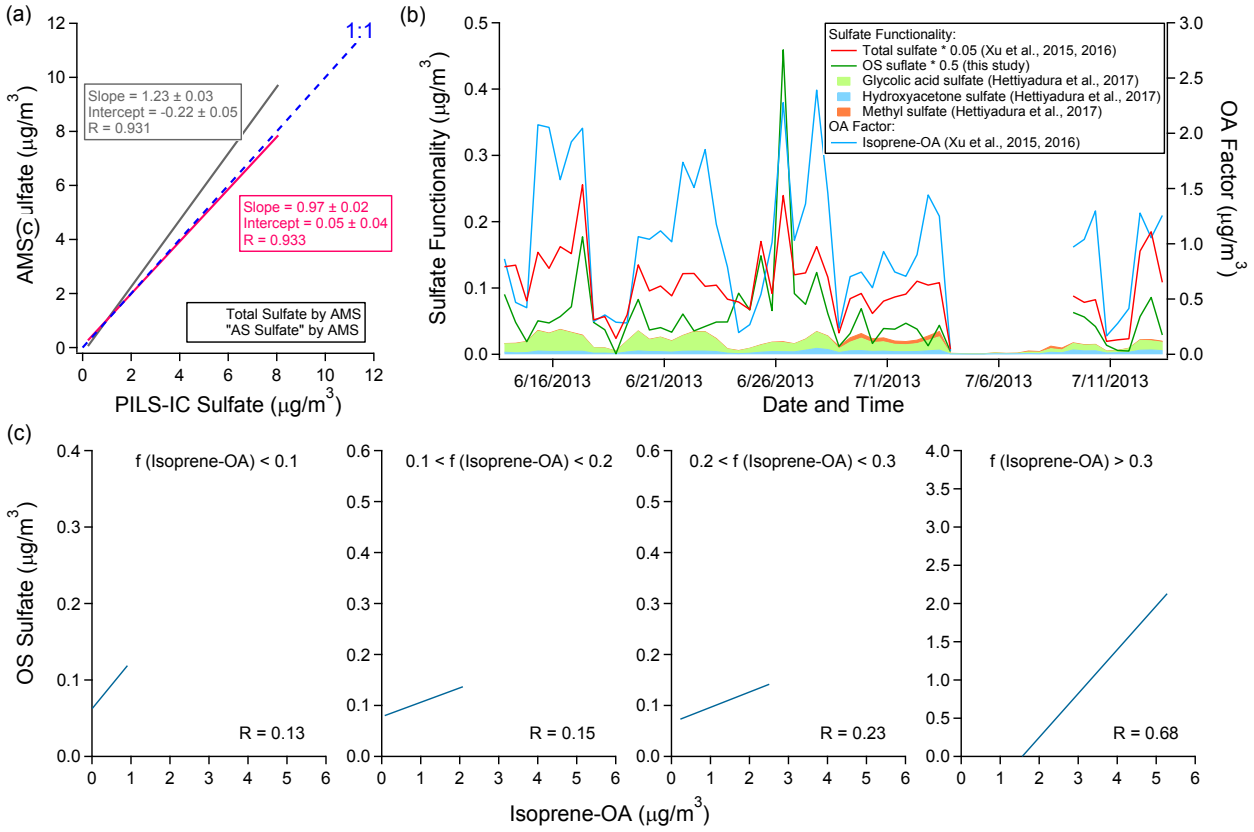
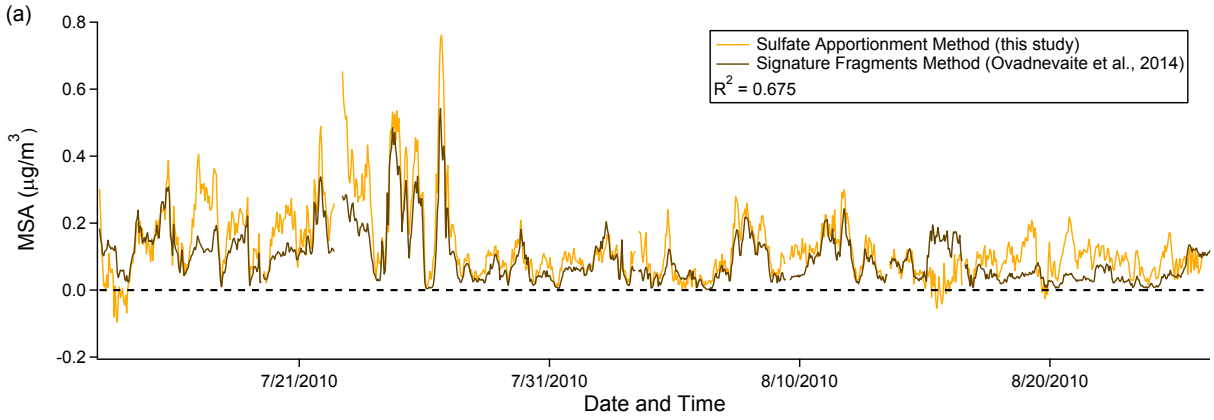


Figure 4 (a) Comparison of AMS total sulfate and AMS "AS sulfate" (calculated by sulfate apportionment method) with PM_1 inorganic sulfate (measured by PILS-IC). (b) Time series of total sulfate (measured by the AMS), "OS sulfate" (calculated by sulfate apportionment method), sulfate functionality concentration of main organosulfur compounds (measured by offline HILIC–TQD), and isoprene-OA factor (resolved by PMF). (c) Comparison of "OS sulfate" with isoprene-OA. The Pearson's R is obtained by linear least-squares fit.

476



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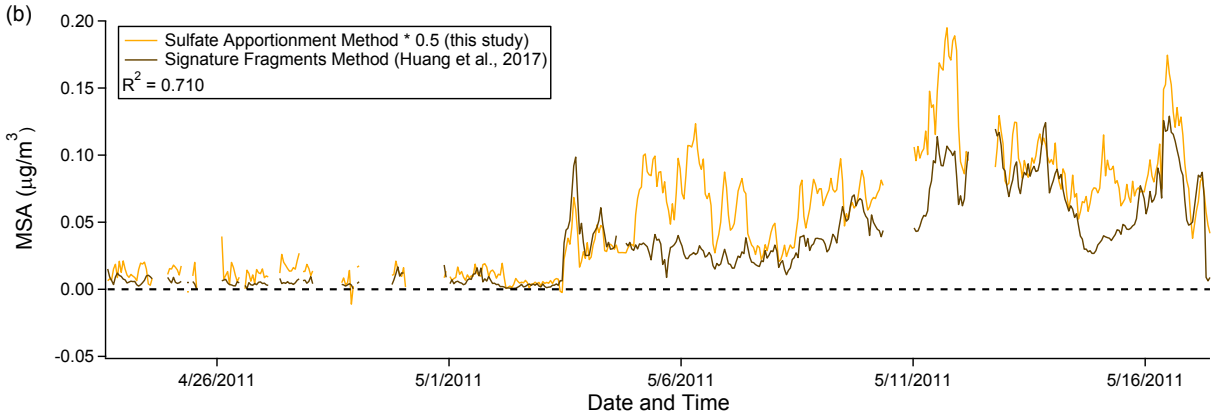

478 **Figure 5** Comparison of MSA mass concentration estimated by sulfate apportionment
479 method and signature fragments method for (a) Mace Head measurements and (b)
480 Polarstern measurements. The Pearson's R is obtained by linear least-squares fit.

481

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Supporting Information

Brief descriptions of uncertainty analysis and UMR analysis, details of standard compounds characterization, and supplementary figures

REFERENCES

1. Liggio, J.; Li, S.-M., Organosulfate formation during the uptake of pinonaldehyde on acidic sulfate aerosols. *Geophysical Research Letters* **2006,** *33*, (13), L13808.
2. Surratt, J. D.; Kroll, J. H.; Kleindienst, T. E.; Edney, E. O.; Claeys, M.; Sorooshian, A.; Ng, N. L.; Offenberg, J. H.; Lewandowski, M.; Jaoui, M.; Flagan, R. C.; Seinfeld, J. H., Evidence for Organosulfates in Secondary Organic Aerosol. *Environmental Science & Technology* **2007,** *41*, (2), 517-527.
3. Surratt, J. D.; Gómez-González, Y.; Chan, A. W. H.; Vermeylen, R.; Shahgholi, M.; Kleindienst, T. E.; Edney, E. O.; Offenberg, J. H.; Lewandowski, M.; Jaoui, M.; Maenhaut, W.; Claeys, M.; Flagan, R. C.; Seinfeld, J. H., Organosulfate Formation in Biogenic Secondary Organic Aerosol. *The Journal of Physical Chemistry A* **2008,** *112*, (36), 8345-8378.
4. Riva, M.; Tomaz, S.; Cui, T.; Lin, Y.-H.; Perraudin, E.; Gold, A.; Stone, E. A.; Villenave, E.; Surratt, J. D., Evidence for an Unrecognized Secondary Anthropogenic Source of Organosulfates and Sulfonates: Gas-Phase Oxidation of Polycyclic Aromatic Hydrocarbons in the Presence of Sulfate Aerosol. *Environmental Science & Technology* **2015,** *49*, (11), 6654-6664.
5. Stone, E. A.; Yang, L.; Yu, L. E.; Rupakheti, M., Characterization of organosulfates in atmospheric aerosols at Four Asian locations. *Atmospheric Environment* **2012,** *47*, 323-329.
6. Tolocka, M. P.; Turpin, B., Contribution of Organosulfur Compounds to Organic Aerosol Mass. *Environmental Science & Technology* **2012,** *46*, (15), 7978-7983.
7. Iinuma, Y.; Müller, C.; Böge, O.; Gnauk, T.; Herrmann, H., The formation of organic sulfate esters in the limonene ozonolysis secondary organic aerosol (SOA) under acidic conditions. *Atmospheric Environment* **2007,** *41*, (27), 5571-5583.
8. Iinuma, Y.; Müller, C.; Berndt, T.; Böge, O.; Claeys, M.; Herrmann, H., Evidence for the Existence of Organosulfates from β-Pinene Ozonolysis in Ambient Secondary Organic Aerosol. *Environmental Science & Technology* **2007,** *41*, (19), 6678-6683.
9. Liao, J.; Froyd, K. D.; Murphy, D. M.; Keutsch, F. N.; Yu, G.; Wennberg, P. O.; St. Clair, J. M.; Crounse, J. D.; Wisthaler, A.; Mikoviny, T.; Jimenez, J. L.; Campuzano-Jost, P.; Day, D. A.; Hu, W.; Ryerson, T. B.; Pollack, I. B.; Peischl, J.; Anderson, B. E.; Ziemba, L. D.; Blake, D. R.; Meinardi, S.; Diskin, G., Airborne measurements of organosulfates over the continental U.S. *Journal of Geophysical Research: Atmospheres* **2015,** *120*, (7), 2990-3005.
10. Olson, C. N.; Galloway, M. M.; Yu, G.; Hedman, C. J.; Lockett, M. R.; Yoon, T.; Stone, E. A.; Smith, L. M.; Keutsch, F. N., Hydroxycarboxylic Acid-Derived Organosulfates: Synthesis, Stability, and Quantification in Ambient Aerosol. *Environmental Science & Technology* **2011,** *45*, (15), 6468-6474.
11. Darer, A. I.; Cole-Filipiak, N. C.; O'Connor, A. E.; Elrod, M. J., Formation and Stability of Atmospherically Relevant Isoprene-Derived Organosulfates and Organonitrates. *Environmental Science & Technology* **2011,** *45*, (5), 1895-1902.
12. Tao, S.; Lu, X.; Levac, N.; Bateman, A. P.; Nguyen, T. B.; Bones, D. L.; Nizkorodov, S. A.; Laskin, J.; Laskin, A.; Yang, X., Molecular Characterization of Organosulfates in Organic Aerosols from Shanghai and Los Angeles Urban Areas by Nanospray-Desorption Electrospray Ionization High-Resolution Mass Spectrometry. *Environmental Science & Technology* **2014,** *48*, (18), 10993-11001.

544 13. Estillore, A. D.; Hettiyadura, A. P. S.; Qin, Z.; Leckrone, E.; Wombacher, B.; Humphry,
545 T.; Stone, E. A.; Grassian, V. H., Water Uptake and Hygroscopic Growth of Organosulfate
546 Aerosol. *Environmental Science & Technology* **2016,** *50*, (8), 4259-4268.
547 14. McNeill, V. F.; Woo, J. L.; Kim, D. D.; Schwier, A. N.; Wannell, N. J.; Sumner, A. J.;
548 Barakat, J. M., Aqueous-Phase Secondary Organic Aerosol and Organosulfate Formation in
549 Atmospheric Aerosols: A Modeling Study. *Environmental Science & Technology* **2012,** *46*, (15),
550 8075-8081.
551 15. Maria, S. F.; Russell, L. M.; Turpin, B. J.; Porcja, R. J.; Campos, T. L.; Weber, R. J.;
552 Huebert, B. J., Source signatures of carbon monoxide and organic functional groups in Asian
553 Pacific Regional Aerosol Characterization Experiment (ACE-Asia) submicron aerosol types.
554 *Journal of Geophysical Research: Atmospheres* **2003,** *108*, (D23), n/a-n/a.
555 16. Sorooshian, A.; Crosbie, E.; Maudlin, L. C.; Youn, J.-S.; Wang, Z.; Shingler, T.; Ortega,
556 A. M.; Hersey, S.; Woods, R. K., Surface and Airborne Measurements of Organosulfur and
557 Methanesulfonate Over the Western United States and Coastal Areas. *Journal of geophysical*
558 *research. Atmospheres : JGR* **2015,** *120*, (16), 8535-8548.
559 17. Lukács, H.; Gelencsér, A.; Hoffer, A.; Kiss, G.; Horváth, K.; Hartyáni, Z., Quantitative
560 assessment of organosulfates in size-segregated rural fine aerosol. *Atmos. Chem. Phys.* **2009,** *9*,
561 (1), 231-238.
562 18. Hettiyadura, A. P. S.; Stone, E. A.; Kundu, S.; Baker, Z.; Geddes, E.; Richards, K.;
563 Humphry, T., Determination of atmospheric organosulfates using HILIC chromatography with
564 MS detection. *Atmos. Meas. Tech.* **2015,** *8*, (6), 2347-2358.
565 19. Froyd, K. D.; Murphy, S. M.; Murphy, D. M.; de Gouw, J. A.; Eddingsaas, N. C.;
566 Wennberg, P. O., Contribution of isoprene-derived organosulfates to free tropospheric aerosol
567 mass. *Proceedings of the National Academy of Sciences* **2010,** *107*, (50), 21360-21365.
568 20. Murphy, D. M., The design of single particle laser mass spectrometers. *Mass*
569 *Spectrometry Reviews* **2007,** *26*, (2), 150-165.
570 21. Huang, D. D.; Li, Y. J.; Lee, B. P.; Chan, C. K., Analysis of Organic Sulfur Compounds
571 in Atmospheric Aerosols at the HKUST Supersite in Hong Kong Using HR-ToF-AMS.
572 *Environmental Science & Technology* **2015,** *49*, (6), 3672-3679.
573 22. Farmer, D. K.; Matsunaga, A.; Docherty, K. S.; Surratt, J. D.; Seinfeld, J. H.; Ziemann, P.
574 J.; Jimenez, J. L., Response of an aerosol mass spectrometer to organonitrates and organosulfates
575 and implications for atmospheric chemistry. *Proceedings of the National Academy of Sciences*
576 **2010,** *107*, (15), 6670-6675.
577 23. Docherty, K. S.; Aiken, A. C.; Huffman, J. A.; Ulbrich, I. M.; DeCarlo, P. F.; Sueper, D.;
578 Worsnop, D. R.; Snyder, D. C.; Peltier, R. E.; Weber, R. J.; Grover, B. D.; Eatough, D. J.;
579 Williams, B. J.; Goldstein, A. H.; Ziemann, P. J.; Jimenez, J. L., The 2005 Study of Organic
580 Aerosols at Riverside (SOAR-1): instrumental intercomparisons and fine particle composition.
581 *Atmospheric Chemistry and Physics* **2011,** *11*, (23), 12387-12420.
582 24. Facchini, M. C.; Decesari, S.; Rinaldi, M.; Carbone, C.; Finessi, E.; Mircea, M.; Fuzzi,
583 S.; Moretti, F.; Tagliavini, E.; Ceburnis, D.; O'Dowd, C. D., Important Source of Marine
584 Secondary Organic Aerosol from Biogenic Amines. *Environmental Science & Technology* **2008,**
585 *42*, (24), 9116-9121.
586 25. Ovadnevaite, J.; Ceburnis, D.; Leinert, S.; Dall'Osto, M.; Canagaratna, M.; O'Doherty, S.;
587 Berresheim, H.; O'Dowd, C., Submicron NE Atlantic marine aerosol chemical composition and
588 abundance: Seasonal trends and air mass categorization. *Journal of Geophysical Research:*
589 *Atmospheres* **2014,** *119*, (20), 11,850-11,863.

26. Phinney, L.; Richard Leaitch, W.; Lohmann, U.; Boudries, H.; Worsnop, D. R.; Jayne, J. T.; Toom-Sauntry, D.; Wadleigh, M.; Sharma, S.; Shantz, N., Characterization of the aerosol over the sub-arctic north east Pacific Ocean. *Deep Sea Research Part II: Topical Studies in Oceanography* **2006,** *53*, (20–22), 2410-2433.
27. Zorn, S. R.; Drewnick, F.; Schott, M.; Hoffmann, T.; Borrmann, S., Characterization of the South Atlantic marine boundary layer aerosol using an aerodyne aerosol mass spectrometer. *Atmos. Chem. Phys.* **2008,** *8*, (16), 4711-4728.
28. Ge, X.; Zhang, Q.; Sun, Y.; Ruehl, C. R.; Setyan, A., Effect of aqueous-phase processing on aerosol chemistry and size distributions in Fresno, California, during wintertime. *Environmental Chemistry* **2012,** *9*, (3), 221-235.
29. Huang, S.; Poulain, L.; van Pinxteren, D.; van Pinxteren, M.; Wu, Z.; Herrmann, H.; Wiedensohler, A., Latitudinal and Seasonal Distribution of Particulate MSA over the Atlantic using a Validated Quantification Method with HR-ToF-AMS. *Environmental Science & Technology* **2017,** *51*, (1), 418-426.
30. Willis, M. D.; Burkart, J.; Thomas, J. L.; Kollner, F.; Schneider, J.; Bozem, H.; Hoor, P. M.; Aliabadi, A. A.; Schulz, H.; Herber, A. B.; Leaitch, W. R.; Abbatt, J. P. D., Growth of nucleation mode particles in the summertime Arctic: a case study. *Atmospheric Chemistry and Physics* **2016,** *16*, (12), 7663-7679.
31. Oae, S., *Organic sulfur chemistry: structure and mechanism*. Boca Raton, Fla. : CRC Press: Boca Raton, Fla., 1991.
32. Staudt, S.; Kundu, S.; Lehmler, H.-J.; He, X.; Cui, T.; Lin, Y.-H.; Kristensen, K.; Glasius, M.; Zhang, X.; Weber, R. J.; Surratt, J. D.; Stone, E. A., Aromatic organosulfates in atmospheric aerosols: Synthesis, characterization, and abundance. *Atmospheric Environment* **2014,** *94*, 366-373.
33. Huang, R. J.; Cao, J. J.; Chen, Y.; Yang, L.; Shen, J. C.; You, Q. H.; Wang, K.; Lin, C. S.; Xu, W.; Gao, B.; Li, Y. J.; Chen, Q.; Hoffmann, T.; O'Dowd, C. D.; Bilde, M.; Glasius, M., Organosulfates in atmospheric aerosol: synthesis and quantitative analysis of PM2.5 from Xi'an, northwestern China. *Atmospheric Measurement Techniques* **2018,** *11*, (6), 3447-3456.
34. Hogrefe, O.; Drewnick, F.; Lala, G. G.; Schwab, J. J.; Demerjian, K. L., Development, operation and applications of an aerosol generation, calibration and research facility. *Aerosol Science and Technology* **2004,** *38*, 196-214.
35. Canagaratna, M.; Jayne, J.; Jimenez, J.; Allan, J.; Alfarra, M.; Zhang, Q.; Onasch, T.; Drewnick, F.; Coe, H.; Middlebrook, A., Chemical and microphysical characterization of ambient aerosols with the aerodyne aerosol mass spectrometer. *Mass Spectrometry Reviews* **2007,** *26*, (2), 185-222.
36. Sanderson, R. T., *Chemical bonds and bond energy*. New York, Academic Press: New York, 1971.
37. Allan, J. D.; Delia, A. E.; Coe, H.; Bower, K. N.; Alfarra, M. R.; Jimenez, J. L.; Middlebrook, A. M.; Drewnick, F.; Onasch, T. B.; Canagaratna, M. R.; Jayne, J. T.; Worsnop, D. R., A generalised method for the extraction of chemically resolved mass spectra from Aerodyne aerosol mass spectrometer data. *Journal of Aerosol Science* **2004,** *35*, (7), 909-922.
38. Allan, J. D.; Bower, K. N.; Coe, H.; Boudries, H.; Jayne, J. T.; Canagaratna, M. R.; Millet, D. B.; Goldstein, A. H.; Quinn, P. K.; Weber, R. J.; Worsnop, D. R., Submicron aerosol composition at Trinidad Head, California, during ITCT 2K2: Its relationship with gas phase volatile organic carbon and assessment of instrument performance. *Journal of Geophysical Research: Atmospheres* **2004,** *109*, (D23), n/a-n/a.

39. Hu, W.; Campuzano-Jost, P.; Day, D. A.; Croteau, P.; Canagaratna, M. R.; Jayne, J. T.; Worsnop, D. R.; Jimenez, J. L., Evaluation of the new capture vapourizer for aerosol mass spectrometers (AMS) through laboratory studies of inorganic species. *Atmos. Meas. Tech.* **2017,** *10*, (8), 2897-2921.

40. Aiken, A. C.; DeCarlo, P. F.; Jimenez, J. L., Elemental Analysis of Organic Species with Electron Ionization High-Resolution Mass Spectrometry. *Analytical Chemistry* **2007,** *79*, (21), 8350-8358.

41. Aiken, A. C.; DeCarlo, P. F.; Kroll, J. H.; Worsnop, D. R.; Huffman, J. A.; Docherty, K. S.; Ulbrich, I. M.; Mohr, C.; Kimmel, J. R.; Sueper, D.; Sun, Y.; Zhang, Q.; Trimborn, A.; Northway, M.; Ziemann, P. J.; Canagaratna, M. R.; Onasch, T. B.; Alfarra, M. R.; Prevot, A. S. H.; Dommen, J.; Duplissy, J.; Metzger, A.; Baltensperger, U.; Jimenez, J. L., O/C and OM/OC Ratios of Primary, Secondary, and Ambient Organic Aerosols with High-Resolution Time-of-Flight Aerosol Mass Spectrometry. *Environmental Science & Technology* **2008,** *42*, (12), 4478-4485.

42. Shiraiwa, M.; Li, Y.; Tsimpidi, A. P.; Karydis, V. A.; Berkemeier, T.; Pandis, S. N.; Lelieveld, J.; Koop, T.; Poschl, U., Global distribution of particle phase state in atmospheric secondary organic aerosols. *Nature Communications* **2017,** *8*, 7.

43. DeRieux, W. S. W.; Li, Y.; Lin, P.; Laskin, J.; Laskin, A.; Bertram, A. K.; Nizkorodov, S. A.; Shiraiwa, M., Predicting the glass transition temperature and viscosity of secondary organic material using molecular composition. *Atmos. Chem. Phys.* **2018,** *18*, (9), 6331-6351.

44. Matthew, B. M.; Middlebrook, A. M.; Onasch, T. B., Collection Efficiencies in an Aerodyne Aerosol Mass Spectrometer as a Function of Particle Phase for Laboratory Generated Aerosols. *Aerosol Science and Technology* **2008,** *42*, (11), 884-898.

45. Xu, W.; Croteau, P.; Williams, L.; Canagaratna, M.; Onasch, T.; Cross, E.; Zhang, X.; Robinson, W.; Worsnop, D.; Jayne, J., Laboratory characterization of an aerosol chemical speciation monitor with PM2.5 measurement capability. *Aerosol Science and Technology* **2017,** *51*, (1), 69-83.

46. Xu, W.; Lambe, A.; Silva, P.; Hu, W.; Onasch, T.; Williams, L.; Croteau, P.; Zhang, X.; Renbaum-Wolff, L.; Fortner, E.; Jimenez, J. L.; Jayne, J.; Worsnop, D.; Canagaratna, M., Laboratory evaluation of species-dependent relative ionization efficiencies in the Aerodyne Aerosol Mass Spectrometer. *Aerosol Science and Technology* **2018,** *52*, (6), 626-641.

47. Murphy, D. M.; Cziczo, D. J.; Hudson, P. K.; Thomson, D. S., Carbonaceous material in aerosol particles in the lower stratosphere and tropopause region. *Journal of Geophysical Research: Atmospheres* **2007,** *112*, (D4).

48. Guo, H.; Xu, L.; Bougiatioti, A.; Cerully, K. M.; Capps, S. L.; Hite Jr, J. R.; Carlton, A. G.; Lee, S. H.; Bergin, M. H.; Ng, N. L.; Nenes, A.; Weber, R. J., Fine-particle water and pH in the southeastern United States. *Atmos. Chem. Phys.* **2015,** *15*, (9), 5211-5228.

49. Drewnick, F.; Diesch, J. M.; Faber, P.; Borrmann, S., Aerosol mass spectrometry: particle–vaporizer interactions and their consequences for the measurements. *Atmos. Meas. Tech.* **2015,** *8*, (9), 3811-3830.

50. Schroder, J. C.; Campuzano-Jost, P.; Day, D. A.; Shah, V.; Larson, K.; Sommers, J. M.; Sullivan, A. P.; Campos, T.; Reeves, J. M.; Hills, A.; Hornbrook, R. S.; Blake, N. J.; Scheuer, E.; Guo, H.; Fibiger, D. L.; McDuffie, E. E.; Hayes, P. L.; Weber, R. J.; Dibb, J. E.; Apel, E. C.; Jaeglé, L.; Brown, S. S.; Thornton, J. A.; Jimenez, J. L., Sources and Secondary Production of Organic Aerosols in the Northeastern United States during WINTER. *Journal of Geophysical Research: Atmospheres* **2018,** *123*, (14), 7771-7796.

682 51. Clegg, S. L.; Brimblecombe, P.; Wexler, A. S., Thermodynamic model of the system H+-
683 NH_4^+-SO_4^{2-}-NO_3^--H_2O at tropospheric temperatures. *Journal of Physical Chemistry A* **1998,** *102*,
684 (12), 2137-2154.
685 52. Wexler, A. S.; Clegg, S. L., Atmospheric aerosol models for systems including the ions
686 H^+, NH_4^+, Na^+, SO_4^{2-}, NO_3^-,Cl^-, Br^-, and H_2O. *Journal of Geophysical Research-Atmospheres*
687 **2002,** *107*, (D14), 14.
688 53. Clegg, S. L.; Seinfeld, J. H.; Edney, E. O., Thermodynamic modelling of aqueous
689 aerosols containing electrolytes and dissolved organic compounds. II. An extended Zdanovskii-
690 Stokes-Robinson approach. *Journal of Aerosol Science* **2003,** *34*, (6), 667-690.
691 54. Zhang, Q.; Jimenez, J. L.; Worsnop, D. R.; Canagaratna, M., A Case Study of Urban
692 Particle Acidity and Its Influence on Secondary Organic Aerosol. *Environmental Science &*
693 *Technology* **2007,** *41*, (9), 3213-3219.
694 55. Bougiatioti, A.; Nikolaou, P.; Stavroulas, I.; Kouvarakis, G.; Weber, R.; Nenes, A.;
695 Kanakidou, M.; Mihalopoulos, N., Particle water and pH in the eastern Mediterranean: source
696 variability and implications for nutrient availability. *Atmos. Chem. Phys.* **2016,** *16*, (7), 4579-
697 4591.
698 56. Guo, H.; Weber, R. J.; Nenes, A., High levels of ammonia do not raise fine particle pH
699 sufficiently to yield nitrogen oxide-dominated sulfate production. *Scientific Reports* **2017,** *7*, (1),
700 12109.
701 57. Liu, M.; Song, Y.; Zhou, T.; Xu, Z.; Yan, C.; Zheng, M.; Wu, Z.; Hu, M.; Wu, Y.; Zhu,
702 T., Fine particle pH during severe haze episodes in northern China. *Geophysical Research*
703 *Letters* **2017,** *44*, (10), 5213-5221.
704 58. Guo, H.; Liu, J.; Froyd, K. D.; Roberts, J. M.; Veres, P. R.; Hayes, P. L.; Jimenez, J. L.;
705 Nenes, A.; Weber, R. J., Fine particle pH and gas–particle phase partitioning of inorganic species
706 in Pasadena, California, during the 2010 CalNex campaign. *Atmos. Chem. Phys.* **2017,** *17*, (9),
707 5703-5719.
708 59. Surratt, J. D.; Chan, A. W.; Eddingsaas, N. C.; Chan, M.; Loza, C. L.; Kwan, A. J.;
709 Hersey, S. P.; Flagan, R. C.; Wennberg, P. O.; Seinfeld, J. H., Reactive intermediates revealed in
710 secondary organic aerosol formation from isoprene. *Proceedings of the National Academy of*
711 *Sciences* **2010,** *107*, (15), 6640-6645.
712 60. Tuet, W. Y.; Chen, Y.; Xu, L.; Fok, S.; Gao, D.; Weber, R. J.; Ng, N. L., Chemical
713 oxidative potential of secondary organic aerosol (SOA) generated from the photooxidation of
714 biogenic and anthropogenic volatile organic compounds. *Atmos. Chem. Phys.* **2017,** *17*, (2), 839-
715 853.
716 61. Docherty, K. S.; Jaoui, M.; Corse, E.; Jimenez, J. L.; Offenberg, J. H.; Lewandowski, M.;
717 Kleindienst, T. E., Collection Efficiency of the Aerosol Mass Spectrometer for Chamber-
718 Generated Secondary Organic Aerosols. *Aerosol Science and Technology* **2013,** *47*, (3), 294-309.
719 62. Bahreini, R.; Keywood, M. D.; Ng, N. L.; Varutbangkul, V.; Gao, S.; Flagan, R. C.;
720 Seinfeld, J. H.; Worsnop, D. R.; Jimenez, J. L., Measurements of Secondary Organic Aerosol
721 from Oxidation of Cycloalkenes, Terpenes, and m-Xylene Using an Aerodyne Aerosol Mass
722 Spectrometer. *Environmental Science & Technology* **2005,** *39*, (15), 5674-5688.
723 63. Lin, Y.-H.; Zhang, Z.; Docherty, K. S.; Zhang, H.; Budisulistiorini, S. H.; Rubitschun, C.
724 L.; Shaw, S. L.; Knipping, E. M.; Edgerton, E. S.; Kleindienst, T. E.; Gold, A.; Surratt, J. D.,
725 Isoprene Epoxydiols as Precursors to Secondary Organic Aerosol Formation: Acid-Catalyzed
726 Reactive Uptake Studies with Authentic Compounds. *Environmental Science & Technology*
727 **2012,** *46*, (1), 250-258.

64. Riedel, T. P.; Lin, Y. H.; Zhang, Z.; Chu, K.; Thornton, J. A.; Vizuete, W.; Gold, A.; Surratt, J. D., Constraining condensed-phase formation kinetics of secondary organic aerosol components from isoprene epoxydiols. *Atmos. Chem. Phys.* **2016,** *16*, (3), 1245-1254.
65. Zhang, Y.; Chen, Y.; Lambe, A. T.; Olson, N. E.; Lei, Z.; Craig, R. L.; Zhang, Z.; Gold, A.; Onasch, T. B.; Jayne, J. T.; Worsnop, D. R.; Gaston, C. J.; Thornton, J. A.; Vizuete, W.; Ault, A. P.; Surratt, J. D., Effect of the Aerosol-Phase State on Secondary Organic Aerosol Formation from the Reactive Uptake of Isoprene-Derived Epoxydiols (IEPOX). *Environmental Science & Technology Letters* **2018,** *5*, (3), 167-174.
66. Cui, T.; Zeng, Z.; dos Santos, E. O.; Zhang, Z.; Chen, Y.; Zhang, Y.; Rose, C. A.; Budisulistiorini, S. H.; Collins, L. B.; Bodnar, W. M.; de Souza, R. A. F.; Martin, S. T.; Machado, C. M. D.; Turpin, B. J.; Gold, A.; Ault, A. P.; Surratt, J. D., Development of a hydrophilic interaction liquid chromatography (HILIC) method for the chemical characterization of water-soluble isoprene epoxydiol (IEPOX)-derived secondary organic aerosol. *Environmental Science: Processes & Impacts* **2018,** *20*, (11), 1524-1536.
67. Hu, W. W.; Campuzano-Jost, P.; Palm, B. B.; Day, D. A.; Ortega, A. M.; Hayes, P. L.; Krechmer, J. E.; Chen, Q.; Kuwata, M.; Liu, Y. J.; de Sá, S. S.; McKinney, K.; Martin, S. T.; Hu, M.; Budisulistiorini, S. H.; Riva, M.; Surratt, J. D.; St. Clair, J. M.; Isaacman-Van Wertz, G.; Yee, L. D.; Goldstein, A. H.; Carbone, S.; Brito, J.; Artaxo, P.; de Gouw, J. A.; Koss, A.; Wisthaler, A.; Mikoviny, T.; Karl, T.; Kaser, L.; Jud, W.; Hansel, A.; Docherty, K. S.; Alexander, M. L.; Robinson, N. H.; Coe, H.; Allan, J. D.; Canagaratna, M. R.; Paulot, F.; Jimenez, J. L., Characterization of a real-time tracer for isoprene epoxydiols-derived secondary organic aerosol (IEPOX-SOA) from aerosol mass spectrometer measurements. *Atmos. Chem. Phys.* **2015,** *15*, (20), 11807-11833.
68. Hettiyadura, A. P. S.; Jayarathne, T.; Baumann, K.; Goldstein, A. H.; de Gouw, J. A.; Koss, A.; Keutsch, F. N.; Skog, K.; Stone, E. A., Qualitative and quantitative analysis of atmospheric organosulfates in Centreville, Alabama. *Atmos. Chem. Phys.* **2017,** *17*, (2), 1343-1359.
69. Xu, L.; Guo, H.; Boyd, C. M.; Klein, M.; Bougiatioti, A.; Cerully, K. M.; Hite, J. R.; Isaacman-VanWertz, G.; Kreisberg, N. M.; Knote, C.; Olson, K.; Koss, A.; Goldstein, A. H.; Hering, S. V.; de Gouw, J.; Baumann, K.; Lee, S. H.; Nenes, A.; Weber, R. J.; Ng, N. L., Effects of anthropogenic emissions on aerosol formation from isoprene and monoterpenes in the southeastern United States. *Proceedings of the National Academy of Sciences* **2015,** *112*, (1), 37-42.
70. Xu, L.; Suresh, S.; Guo, H.; Weber, R. J.; Ng, N. L., Aerosol characterization over the southeastern United States using high-resolution aerosol mass spectrometry: spatial and seasonal variation of aerosol composition and sources with a focus on organic nitrates. *Atmos. Chem. Phys.* **2015,** *15*, (13), 7307-7336.
71. Allen, H. M.; Draper, D. C.; Ayres, B. R.; Ault, A.; Bondy, A.; Takahama, S.; Modini, R. L.; Baumann, K.; Edgerton, E.; Knote, C.; Laskin, A.; Wang, B.; Fry, J. L., Influence of crustal dust and sea spray supermicron particle concentrations and acidity on inorganic NO_3^- aerosol during the 2013 Southern Oxidant and Aerosol Study. *Atmos. Chem. Phys.* **2015,** *15*, (18), 10669-10685.
72. Hettiyadura, A. P. S.; Xu, L.; Jayarathne, T.; Skog, K.; Guo, H.; Weber, R. J.; Nenes, A.; Keutsch, F. N.; Ng, N. L.; Stone, E. A., Source apportionment of organic carbon in Centreville, AL using organosulfates in organic tracer-based positive matrix factorization. *Atmospheric Environment* **2018,** *186*, 74-88.

774 73. Fridlind, A. M.; Jacobson, M. Z., A study of gas-aerosol equilibrium and aerosol pH in
775 the remote marine boundary layer during the First Aerosol Characterization Experiment (ACE
776 1). *Journal of Geophysical Research: Atmospheres* **2000,** *105*, (D13), 17325-17340.
777 74. Keene, W. C.; Pszenny, A. A. P.; Maben, J. R.; Stevenson, E.; Wall, A., Closure
778 evaluation of size-resolved aerosol pH in the New England coastal atmosphere during summer.
779 *Journal of Geophysical Research: Atmospheres* **2004,** *109*, (D23), n/a-n/a.

780